



# Selective oxidation of glycerol to formic acid catalyzed by $\text{Ru}(\text{OH})_4/\text{r-GO}$ in the presence of $\text{FeCl}_3$

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## ABSTRACT

Herein selective oxidation of glycerol to formic acid catalyzed by  $\text{Ru}(\text{OH})_4$  nanoparticles decorated on reduced graphite oxide (r-GO) in the presence of  $\text{FeCl}_3$  was presented. The  $\text{Ru}(\text{OH})_4/\text{r-GO}$  catalyst was prepared via refluxing  $\text{RuCl}_3$  aqueous solution containing graphite oxide (GO), and was characterized by means of transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. It was indicated that Ru species were present in the form of  $\text{Ru}(\text{OH})_4$ , which was uniformly distributed on the r-GO surface with average particle size around 1.3 nm. The as-prepared  $\text{Ru}(\text{OH})_4/\text{r-GO}$  catalyst was used to catalyze the glycerol oxidation in aqueous solutions of Lewis acids (including  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{ZnCl}_2$ ), and the effects of reaction time, temperature (120–180 °C),  $\text{O}_2$  pressure (0.5–1.5 MPa) and  $\text{FeCl}_3$  concentration (5–60 mM) were investigated. It was demonstrated that  $\text{Ru}(\text{OH})_4/\text{r-GO}$  and  $\text{FeCl}_3$  displayed synergistic effect on the production of formic acid from glycerol oxidation in aqueous solution at 160 °C, and high yields of formic acid around 60% were achieved. The possible reaction pathway was discussed. Moreover, the combination of  $\text{Ru}(\text{OH})_4/\text{r-GO}$  and  $\text{FeCl}_3$  was extended to the oxidation of carbohydrates including glucose, fructose and cellulose, and formic acid was obtained in relatively high yields. This study provides an efficient catalytic system for production of formic acid from biomass.

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## 1. Introduction

With the requirements of sustainable development, the production of fuel and chemicals from renewable biomass has been paid more and more attention. Formic acid (FA) is a commodity chemical that is widely used in the chemical, agricultural, textile, leather, pharmaceutical, and rubber industries. More recently, FA is proposed as a suitable hydrogen storage compound since it can be easily and selectively decomposed to hydrogen and  $\text{CO}_2$  through metal catalyzed processes under very mild conditions [1–4]. Therefore, the production of FA from biomass can be considered as a promising alternative route to get hydrogen from the renewable biomass, which has been extensively investigated [5–9].

To date, saccharides such as glucose, fructose and cellulose, have been used as biomass feedstocks to produce FA via oxidation under different conditions. In an earlier report, McGinnis et al. [5] studied the carbohydrate oxidation in water using  $\text{O}_2$  as an oxidant in the temperatures of 170–220 °C. The highest yield of FA from

glucose was 25 mol% in the presence of  $\text{Fe}^{3+}$  as a co-oxidant at 190 °C and 1.5 MPa  $\text{O}_2$  within 30 min. Jin et al. [6] reported that a 75% yield of FA could be attained by using  $\text{H}_2\text{O}_2$  as the oxidant during glucose oxidation, but alkali bases (5 equiv) had to be used to suppress the oxidative decomposition of FA. Recently, Wasserscheid et al. [7] presented a straightforward method to transform carbohydrate-based biomass to FA by oxidation with molecular oxygen in aqueous solution using a Keggin-type  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  polyoxometalate as the catalyst. Several water-soluble carbohydrates including glucose, sorbitol, cellobiose, xylose, sucrose, glycerol, were selectively converted to FA and  $\text{CO}_2$  under very mild conditions. Using the same catalyst, they further converted water-insoluble biomass like wood, waste paper, or even cyanobacteria to FA with *p*-toluenesulfonic acid as the best additive [8].

Glycerol is an easily available feedstock from biodiesel production, and its conversion to value-added chemicals has attracted much attention in recent years. The selective oxidation of glycerol has been widely investigated with focus on producing C3 carbonxylic acids such as glyceric acid [10–12], lactic acid [13,14]. However, the production of FA from glycerol oxidation was seldom reported [15]. The catalysts played crucial role in the production of FA from the biomass oxidation, which generally have the features

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promoting the biomass oxidation to FA and preventing FA further oxidation to CO<sub>2</sub> under the applied conditions. To date, only several catalysts were reported for FA production from biomass oxidation [16]. Therefore, developing efficient catalysts is highly required.

RuO<sub>x</sub> is reported to be an efficient catalyst for aerobic oxidation of alcohols to corresponding aldehydes or carbonxylic acids via oxidative dehydrogenation in aqueous solution with moderate to excellent yields under relatively benign reaction conditions [17,18]. FeCl<sub>3</sub> as a catalyst displays superior performance in biomass pretreatment [19,20]. In this work, we reported an efficient catalytic system for the production of FA from glycerol oxidation. Reduced graphite oxide (r-GO) supported Ru(OH)<sub>4</sub> nanoparticles (denoted as Ru(OH)<sub>4</sub>/r-GO) were prepared via refluxing RuCl<sub>3</sub> aqueous solution containing graphite oxide (GO), which were characterized by means of different techniques including transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS). The as-prepared Ru(OH)<sub>4</sub>/r-GO catalyst was used to catalyze selective oxidation of glycerol to FA in the presence of FeCl<sub>3</sub> in aqueous solution. The influences of reaction temperature, reaction time, O<sub>2</sub> pressure, and FeCl<sub>3</sub> concentration on the glycerol conversion and FA yield were investigated. The reaction pathway for FA production from glycerol oxidation was discussed as well. Moreover, the catalytic system was applied in the oxidation of carbohydrates to produce FA.

## 2. Experimental

### 2.1. Materials

Glycerol, glucose, fructose, cellulose, dihydroxyacetone, glyceraldehyde, glyceric acid, glycolic acid, acetic acid, oxalic acid, formic acid, RuCl<sub>3</sub>·3H<sub>2</sub>O, FeCl<sub>3</sub>, AlCl<sub>3</sub>, CrCl<sub>3</sub>, ZnCl<sub>2</sub> and other chemicals were provided by Beijing Chemical Company, and used as received.

The Ru/C, Pt/C and Pd/C catalysts with the metal mass weight of 5 wt% were purchased from Shaanxi Rock New Materials Co. Ltd, and the metal particle size were 1.6, 2.6 and 2.4 nm, respectively.

### 2.2. Catalyst preparation

The preparation of Ru(OH)<sub>4</sub>/r-GO was based on a reported procedure [21]. Typically, 0.36 g of graphite oxide (GO) was dispersed in 200 mL of H<sub>2</sub>O in a 500 mL round flask under ultrasonication for 5 h to get a uniform brown suspension. Then 15 mL of RuCl<sub>3</sub> solution (containing 0.0786 g of RuCl<sub>3</sub>·3H<sub>2</sub>O) was added into the flask. After being stirred at room temperature for 5 h, the mixture was refluxed in air for 24 h, and the suspension gradually became black. The black solid was collected by centrifugation and washed several times using distilled water, followed by vacuum drying over night at 70 °C.

### 2.3. Catalyst characterization

The morphology of the as-prepared Ru(OH)<sub>4</sub>/r-GO catalyst was examined by means of TEM on a JEOL 2010 transmission electron microscope using an accelerating voltage of 200 kV. For TEM measurement, the samples were ultrasonically dispersed in ethanol and then placed on carbon-coated Cu grids. The particle size distribution was calculated by counting over 200 particles. XPS data were collected on an ESCALab250xi electron spectrometer from Thermo Scientific using 300 W Al Kα radiation. The base pressure was about 1.68 × 10<sup>−9</sup> mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The metal loading content in the samples was determined by ICP-AES (VISTA-MPX). Raman spectra were recorded on a Renishaw-2000 microprobe spectrometer (514 nm, Ar<sup>+</sup> ion laser).

### 2.4. Procedures for glycerol oxidation

The glycerol oxidation reaction was carried out in a 50 mL Teflon-lined stainless steel autoclave. In a typical experiment, glycerol (2 mmol), appropriate amounts of FeCl<sub>3</sub> and Ru(OH)<sub>4</sub>/r-GO were sealed in the reactor. The air inside the reactor was removed by charging oxygen 3 times and then O<sub>2</sub> was charged up to the desired pressure (e.g., 0.5 MPa). The autoclave was then moved to an oil-bath of desired temperature (e.g., 160 °C) and maintained under stirring for the desired reaction time (e.g., 1 h). Subsequently, the vessel was cooled down in ice-water, and vented slowly. The gas products were collected by a gas-ballon and analyzed by GC detected by TCD. The liquid products together with unreacted substrate were collected by removing the solid catalyst via centrifugation, and analyzed by HPLC equipped with UV and RID detectors, using HPX-87H column and sulfuric acid aqueous solution (5 mmol/L) as mobile phase with a 0.6 mL/min flowrate at 55 °C. Glycerol and formaldehyde were detected by RID detector, while the compounds with UV-absorption were detected by UV detector at the wavelength of 210 nm. The work curve for each detected compound was first plotted using corresponding pure compound, which was used to determine the masses of the unreacted glycerol and the obtained products/intermediates. The glycerol conversion and product yields were calculated on a carbon basis and are defined as follows:

conversion (%) =

$$\frac{\text{moles of reactant charged} - \text{moles of reactant left}}{\text{moles of reactant charged}} \times 100$$

$$\text{yield (\%)} = \frac{\text{carbon moles of product}}{\text{carbon moles of reactant charged}} \times 100$$

In addition, the total organic carbon (TOC) in the liquid reaction solution was determined on a Shimadzu TOC-V<sub>CPH</sub> analyzer at 720 °C using Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and NDIR detector. The reaction solution was diluted to 25 mL, and then 1 mL of this solution was diluted 10 times for TOC analysis.

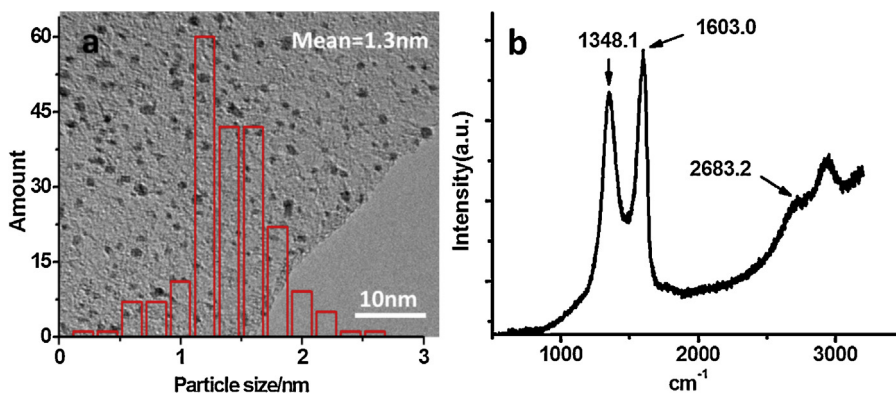
## 3. Results and discussion

### 3.1. Characterization of catalyst

The as-prepared ruthenium catalyst could be well redispersed in water to form relatively stable suspension. The amount of Ru in the catalyst was measured by ICP, which was estimated to be almost identical to the theoretical value of the used Ru. This indicates that the used Ru was almost deposited completely onto the support, which was also confirmed by the fact that no Ru species was detected in the reaction solution for preparing the catalyst.

The microstructure of the catalyst was examined by TEM, and Fig. 1a shows a typical TEM image with particle size distribution obtained from randomly measuring 200 particles. It is clear that numerous nanoparticles were uniformly distributed on the surface of the support with the average particle size around 1.3 nm. The small size and uniform distribution of these particles may be ascribed to the unique natures of the support surface. Fig. 1b shows Raman spectrum of the catalyst, which obviously displays the features of r-GO with D and G peaks at 1348.1 and 1603.0 cm<sup>−1</sup>, respectively. The presence of intense D peak indicates that there were defects and/or functional groups on the surface of the support, which were beneficial to the immobilization of nanoparticle.

The oxidation states of the species in the catalyst were examined by XPS. Fig. 2a illustrates the survey XPS spectrum of the catalyst, which indicates the predominant presence of elements Ru, C, O, and no Cl element was detectable. This suggests that RuCl<sub>3</sub> was



**Fig. 1.** Characterization of the catalyst: (a) TEM image and particle size distribution, 200 particles were randomly measured for particle size distribution. (b) Raman spectrum.

converted into Ru oxide during the synthesis of the catalyst. Fig. 2b shows the Ru3p XPS spectrum, in which an intense peak appeared at binding energy (BE) of 463.6 eV, attributing to  $\text{Ru}^{4+}\text{-O}$  species. This suggests that the  $\text{Ru}^{3+}$  was oxidized into  $\text{Ru}^{4+}$  in the form of oxide during the catalyst preparation process. In the O1s spectrum (Fig. 2c) the wide peak could be deconvoluted into three peaks with BEs at 533.3, 532.4 and 531.7 eV, which were ascribed to O from  $\text{-C=O}$  of  $\text{-COOH}$ ,  $\text{-C-OH}$  and metal hydroxide, respectively. The groups of  $\text{-COOH}$  and  $\text{-C-OH}$  may be from the r-GO support, which were favorable to immobilizing Ru hydroxide particles onto the r-GO surface. From the XPS analysis, it can be deduced that the ruthenium hydroxide was  $\text{Ru(OH)}_4$ . The catalyst is denoted as  $\text{Ru(OH)}_4/\text{r-GO}$  in this work.

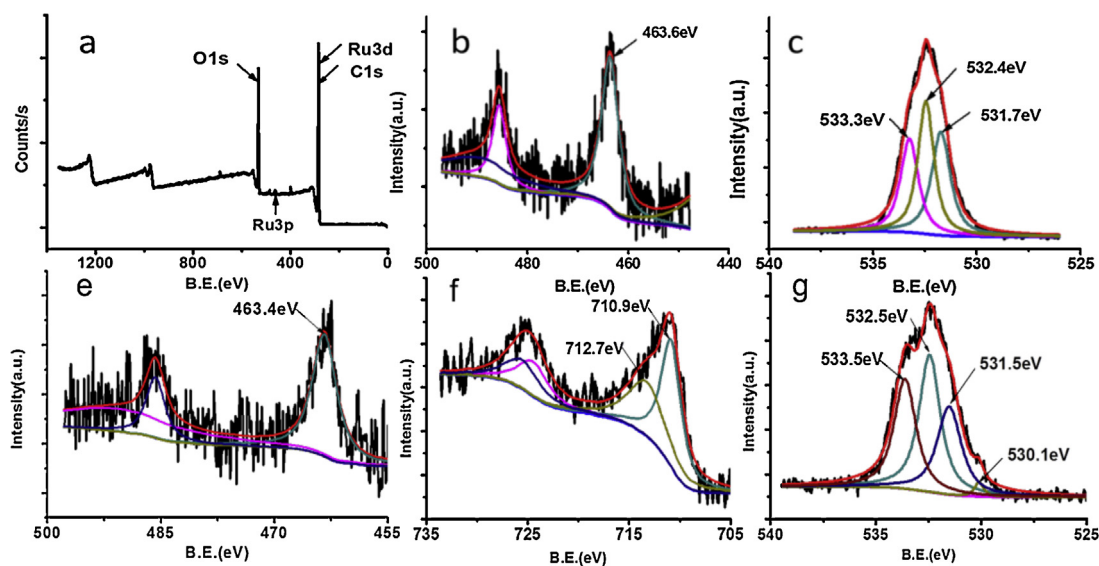
### 3.2. Glycerol oxidation to formic acid

The initial experiments for glycerol oxidation were performed using  $\text{Ru(OH)}_4/\text{r-GO}$  and  $\text{FeCl}_3$  as catalysts, respectively, at  $160^\circ\text{C}$  and  $\text{O}_2$  pressure of 0.5 MPa. It was found that both  $\text{Ru(OH)}_4/\text{r-GO}$  and  $\text{FeCl}_3$  can separately catalyse the glycerol oxidation, and the predominant product in the liquid phase was FA though the glycerol conversion was less than 20% (Table 1, entries 1 and 2). To our delight, the combination of  $\text{Ru(OH)}_4/\text{r-GO}$  and  $\text{FeCl}_3$  significantly improved the glycerol conversion to 95.6% and the FA yield to 53.3% under the same other conditions (Table 1, entry 3), implying that  $\text{Ru(OH)}_4/\text{r-GO}$  and  $\text{FeCl}_3$  generated synergistic effect for the FA

production from the glycerol oxidation. The other compounds detected in the aqueous solution included formaldehyde (FOA), acetic acid (AA) and glycolic acid (GOA), and the overall yields of the products from the aqueous solution reached 74.1% (Table 1, entry 3).  $\text{CO}_2$  was the sole product detected in the gas phase. The TOC analysis for the reaction solution indicated that a trace amount of unknown compounds formed.

To reveal the synergistic effect of  $\text{Ru(OH)}_4/\text{r-GO}$  and  $\text{FeCl}_3$  on glycerol oxidation to FA, the used  $\text{Ru(OH)}_4/\text{r-GO}$  catalyst was examined by ICP and XPS analyses. A trace amount of Fe was detectable by ICP, and the XPS analysis also confirmed the presence of Fe in the used catalyst. In the Fe2p XPS spectrum (Fig. 2f), the peak could be deconvoluted into two peaks with BEs at 710.9 and 712.7 eV, which were ascribed to  $\text{Fe}^{3+}$  in oxide and in chloride, respectively. The iron oxide may result from the slight hydrolysis of  $\text{FeCl}_3$  under the experimental conditions. Compared to that of pure  $\text{FeCl}_3$  (711.8 eV), the Fe2p BE of  $\text{Fe}^{3+}$  in the  $\text{FeCl}_3$  adsorbed onto the GO support shifted to a higher value; meanwhile, the Ru 3p BE (Fig. 2e) shifted to a lower value compared to that in the fresh  $\text{Ru(OH)}_4$  catalyst. The above XPS results indicated that  $\text{Fe}^{3+}$  was adsorbed onto the  $\text{Ru(OH)}_4$  particles during the reaction process, which may be responsible for the synergistic effect on glycerol oxidation to FA.

To explore the effective catalysts for FA production from glycerol oxidation, several Lewis acids including  $\text{AlCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{ZnCl}_2$  were tested. Similar to  $\text{FeCl}_3$ , these Lewis acids showed very low activity for catalyzing glycerol oxidation individually. Interestingly, in



**Fig. 2.** XPS spectra of  $\text{Ru(OH)}_4/\text{r-GO}$  (a–c) and used  $\text{Ru(OH)}_4/\text{r-GO}$  (e–g): (a) survey, (b) Ru3p, (c) O 1s, (e) Ru3p, (f) Fe2p, (g) O 1s.

**Table 1**  
Glycerol oxidation under different conditions<sup>a</sup>.

Entry	Catalyst	Lewis acid	Conv. (%)	Yield (%)					TOC (ppm)
				FA	FOA	AA	GOA	CO <sub>2</sub>	
1	Ru(OH) <sub>4</sub> /r-GO	–	18.4	8.1	ND	2.0	0.9	7.3	266.8
2	–	FeCl <sub>3</sub>	16.6	6.3	1.0	0.3	2.9	5.9	270.7
3	Ru(OH) <sub>4</sub> /r-GO	FeCl <sub>3</sub>	95.6	53.3	15.9	1.0	3.9	20.0	230.3
4	Ru(OH) <sub>4</sub> /r-GO	AlCl <sub>3</sub>	91.6	38.6	3.2	2.8	4.8	31.1	198.0
5	Ru(OH) <sub>4</sub> /r-GO	CrCl <sub>3</sub>	80.3	18.0	2.1	7.3	7.7	40.5	171.2
6	Ru(OH) <sub>4</sub> /r-GO	ZnCl <sub>2</sub>	30.1	9.7	2.5	5.2	2.4	9.3	261.1
7	Ru/C	FeCl <sub>3</sub>	88.2	39.9	10.6	0.9	10.4	25.1	215.5
8	Pd/C	FeCl <sub>3</sub>	67.7	24.9	4.0	1.3	9.3	27.2	209.5
9	Pt/C	FeCl <sub>3</sub>	52.0	18.0	8.3	0.7	7.6	16.8	239.4

<sup>a</sup> Reaction condition: glycerol, 2 mmol; T = 160 °C; reaction time, 1 h; O<sub>2</sub> pressure, 0.5 MPa; glycerol:metal = 1000; Lewis acid concentration, 40 mM.

the cases of Ru(OH)<sub>4</sub>/r-GO combined with these Lewis acids as catalysts, both the glycerol conversion and the FA yield improved considerably compared to the case of Ru(OH)<sub>4</sub>/r-GO as the sole catalyst (Table 1, entries 4–6). This also indicates the synergistic effects between Ru(OH)<sub>4</sub>/r-GO and the Lewis acids. Three commercial metal catalysts, Ru/C, Pd/C and Pt/C with the metal particle size around 2 nm, were also tested in this work. It was demonstrated that Ru/C, Pd/C and Pt/C catalysts could catalyze glycerol oxidation with very low activity and low FA yield in the absence of any Lewis acids (not shown here), while they showed enhanced activity for glycerol conversion in the presence of FeCl<sub>3</sub>, and the FA yield improved as well (Table 1, entries 7–9). From the above findings, it can be deduced that the synergistic effect was generated between the metal catalysts and Lewis acids for the FA production from glycerol oxidation. Among the tested catalysts, the combination of Ru(OH)<sub>4</sub>/r-GO and FeCl<sub>3</sub> exhibited the best performance.

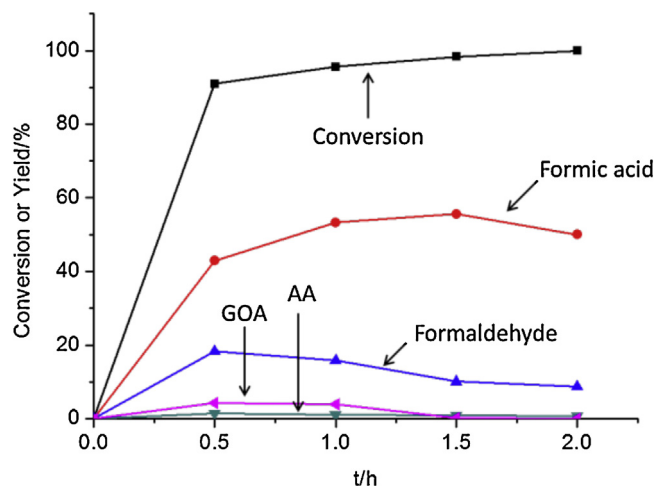
### 3.3. Effects of reaction parameters on glycerol oxidation to formic acid

Used Ru(OH)<sub>4</sub>/r-GO and FeCl<sub>3</sub> as catalysts, the effects of reaction parameters including reaction time, temperature, pressure, FeCl<sub>3</sub> concentration on the glycerol oxidation were investigated. Fig. 3 shows the dependence of the glycerol conversion and the yields of the products and intermediates on reaction time. It was observed that the glycerol conversion reached 90% with the FA yield over 40% at 0.5 h, indicating that the glycerol oxidation occurred rapidly under the experimental conditions. Moreover, all the three intermediates (i.e., GOA, AA and FOA) were present, and formaldehyde showed the highest yield about 20%. Prolonging reaction time to 1 h,

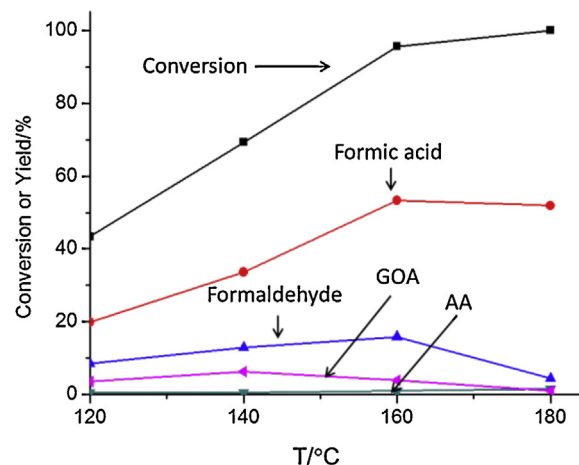
the glycerol conversion approached 100%, and the amounts of FOA and GOA decreased accompanied with the increase in the FA yield. As reaction time prolonged to 2 h, glycerol converted completely, and the FOA yield decreased further with the disappearance of GOA. It should be noticed that the FA yield decreased as well, probably originating from the further oxidation of FA under the experimental conditions.

The effects of reaction temperature on the glycerol oxidation were investigated in the temperature range from 120 to 180 °C, and the results are illustrated in Fig. 4. Higher glycerol conversions were obtained at 160 °C and 180 °C. Glycerol was converted completely within 1 h at 180 °C, but the FA yield was lower slightly than that at 160 °C. As the temperature was reduced to 120 °C, the conversion of glycerol decreased accordingly and the FA yield was only 20%, much lower than that obtained at higher temperatures. These results suggest that high temperature is required for the formation of FA from the oxidation of glycerol using FeCl<sub>3</sub> and Ru(OH)<sub>4</sub>/r-GO as the catalyst. However, when the temperature was too high, for example 180 °C, more FA would be further oxidized to CO<sub>2</sub>, thus resulting in the decline in the FA yield. Therefore, 160 °C was selected as the reaction temperature in this work.

The oxygen pressure is another important factor to influence the selective oxidation of glycerol to FA. In the tested oxygen pressure range of 0–1.5 MPa, both the glycerol conversion and FA yield increased with oxygen pressure in the range of 0–0.5 MPa, and the highest FA yield of 55.1% was achieved at 1.0 MPa, as shown in Fig. 5. Further increasing oxygen pressure to 1.5 MPa, the glycerol conversion almost kept unchanged, while the FA yield slightly declined, probably resulting from the decomposition of FA at higher oxygen pressure.



**Fig. 3.** Dependence of product yields on reaction time. Other reaction conditions: 160 °C, 40 mM FeCl<sub>3</sub>, 0.5 MPa O<sub>2</sub> pressure.



**Fig. 4.** Dependence of glycerol conversion and product yield on the reaction temperature. Other reaction conditions: 1 h, 0.5 MPa O<sub>2</sub> pressure, 40 mM FeCl<sub>3</sub>.



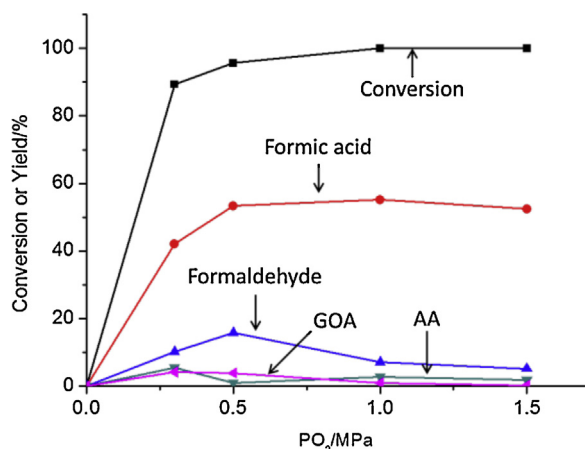


Fig. 5. Dependence of glycerol conversion and product yields on the  $O_2$  pressure. Other reaction conditions:  $160^\circ C$ , 40 mM  $FeCl_3$ , 1 h.

$FeCl_3$  played an important role in the selective oxidation of glycerol to FA. The effect of the  $FeCl_3$  concentration on the glycerol oxidation was investigated in the range of 0–60 mM. It was demonstrated that the presence of  $FeCl_3$  (e.g., 5 mM) in the reaction system significantly improved the glycerol conversion and FA yields, and both increased slightly with the  $FeCl_3$  concentration in the range from 5 to 40, as illustrated in Fig. 6. However, further increasing  $FeCl_3$  concentration to 60 mM resulted in the decrease in the FA yield, which may be ascribed to the further oxidation of FA under this condition.

### 3.4. The possible reaction pathway

To explore the possible reaction pathway of FA formation from glycerol oxidation, the oxidations of the detectable compounds (e.g., FOA, AA, GOA, FA) and possible intermediates of glycerol oxidation were performed under the similar conditions, and the results are listed in Table 2. It was reported that dihydroxyacetone (DHA) and glyceraldehyde (GLYA) were the primary products of glycerol oxidation though they were not detected under the experimental conditions in this work. It was demonstrated that both DHA and GLYA could be rapidly converted to FA with high yields accompanied with FOA, AA and GOA (Table 2, entries 1 and 2), implying that DHA and GLYA might be intermediates of the primary oxidation of glycerol. The GOA oxidation resulted in the production of FOA and FA with a total selectivity around 50%, together with  $CO_2$

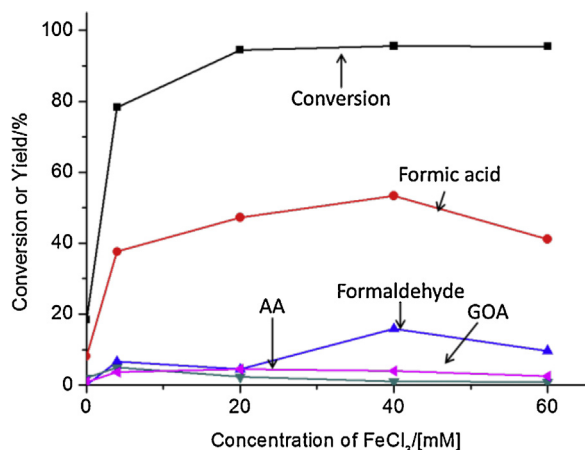


Fig. 6. Dependence of glycerol conversion and product yields on the  $FeCl_3$  concentration. Other reaction conditions:  $160^\circ C$ , 0.5 MPa  $O_2$  pressure, 1 h.

(Table 2, entry 3). Formaldehyde was oxidized to FA with  $CO_2$  as the sole byproduct at a lower oxidation speed compared to that of the glycerol oxidation (Table 2, entry 4). However, AA could not be converted in the presence of  $Ru(OH)_4/r-GO$  and  $FeCl_3$  under the experimental conditions (Table 2, entry 5), indicating that AA was a byproduct instead of intermediate in the glycerol oxidation. In the case of FA oxidation, only 7.7% FA was converted into  $CO_2$  without any other byproduct (Table 2, entry 6). This suggests that FA was relatively stable under the experimental conditions, and that the  $CO_2$  produced in the glycerol oxidation process was not only from the FA oxidation. Oxalic acid (OA) was usually produced in the glycerol oxidation though it was not detected in this work. It was demonstrated that OA could be converted rapidly into  $CO_2$  via oxidation under the experimental conditions (Table 2, entry 7). In addition, no hydrogen was detected in the absence of  $O_2$  under the same other conditions, suggesting that the catalytic system used in this work was not suitable for FA decomposition to  $H_2$ .

Moreover, several control experiments were performed. The oxidations of 1, 2-propylene glycol and 1, 3-propylene glycol were investigated using  $Ru(OH)_4/r-GO$  and  $FeCl_3$  as the catalyst, respectively. It was demonstrated that only a FA yield of 7.7% was obtained as 1, 2-propylene glycol was oxidized while a high FA yield of 50% was obtained from 1, 3-propylene glycol oxidation (Table 2, entries 8 and 9). This means that the pinacol structure may be not necessary in the glycerol oxidation catalyzed by  $Ru(OH)_4/r-GO$  and  $FeCl_3$ , opposite to that reported by Fu and coworkers who found the oxidation catalyzed by  $H_5PV_2Mo_{10}O_{40}$  could not occur without the pinacol structure [16]. It was reported that the two hydroxyl groups in the 1,3-diol structure could be chelated with  $Fe^{3+}$  [22], which may be beneficial to the oxidations of glycerol and 1,3-propylene glycol. The oxidations of ethylene glycol (EG) and glyoxal were also investigated. For the EG oxidation, a low EG conversion and a low FA yield were obtained while a FA yield of 47.2% reached for the glyoxal oxidation (Table 2, entries 10, 11). These results support the hypothesis that the pinacol structure was not necessary, and that the aldehyde groups may be important in the oxidation.

To explore the possible roles of  $Ru(OH)_4/r-GO$  and  $FeCl_3$  in the glycerol oxidation, the oxidations of DHA and GOA were carried out using  $Ru(OH)_4/r-GO$  and  $FeCl_3$  as the separate catalyst. As listed in Table 2 (entries, 12–15), both  $Ru(OH)_4/r-GO$  and  $FeCl_3$  displayed high efficiencies for catalyzing the DHA oxidation with conversion of 100% within 1 h at  $160^\circ C$ , while the product distribution was different considerably. In the case of  $Ru(OH)_4/r-GO$  as the catalyst, the products were complicated. Besides FA, FOA, GOA and AA, other compounds such as glyceric acid and other acids were detected. Moreover, it should be noticed that AA with a high yield of 19.0% was obtained (Table 2, entry 12). Based on these results and the fact that AA was a byproduct and could not be oxidized under the experimental conditions, it can be deduced that  $Ru(OH)_4/r-GO$  tended to catalyze DHA conversion to PA and further to AA and equal FOA via oxidation. In the case of  $FeCl_3$  as the catalyst, FA, FOA, GOA and AA were detected in the liquid products, and their overall yield reached 63.0% with an AA yield of 1.1% (Table 2, entry 13). This indicates that DHA was preferentially converted into GOA and further to FOA and FA in the presence of  $FeCl_3$ , and production of AA was suppressed. GOA was a detectable intermediate in the production of FA. Both  $Ru(OH)_4/r-GO$  and  $FeCl_3$  were effective for catalysing its conversion to FA and FOA, respectively, while their combination showed enhanced performance (Table 2, entries 14 and 15). From the above results, it can be concluded that  $Ru(OH)_4/r-GO$  and  $FeCl_3$  showed synergistic effect on the production of FA from glycerol oxidation, and  $FeCl_3$  suppressed the production of AA as a byproduct.

Based on the above experimental results, we proposed a possible pathway for the FA formation from glycerol oxidation catalyzed by  $Ru(OH)_4/r-GO$  and  $FeCl_3$ , as illustrated in Scheme 1. First, glycerol is catalytically oxidized to DHA and/or GLYA via oxidative

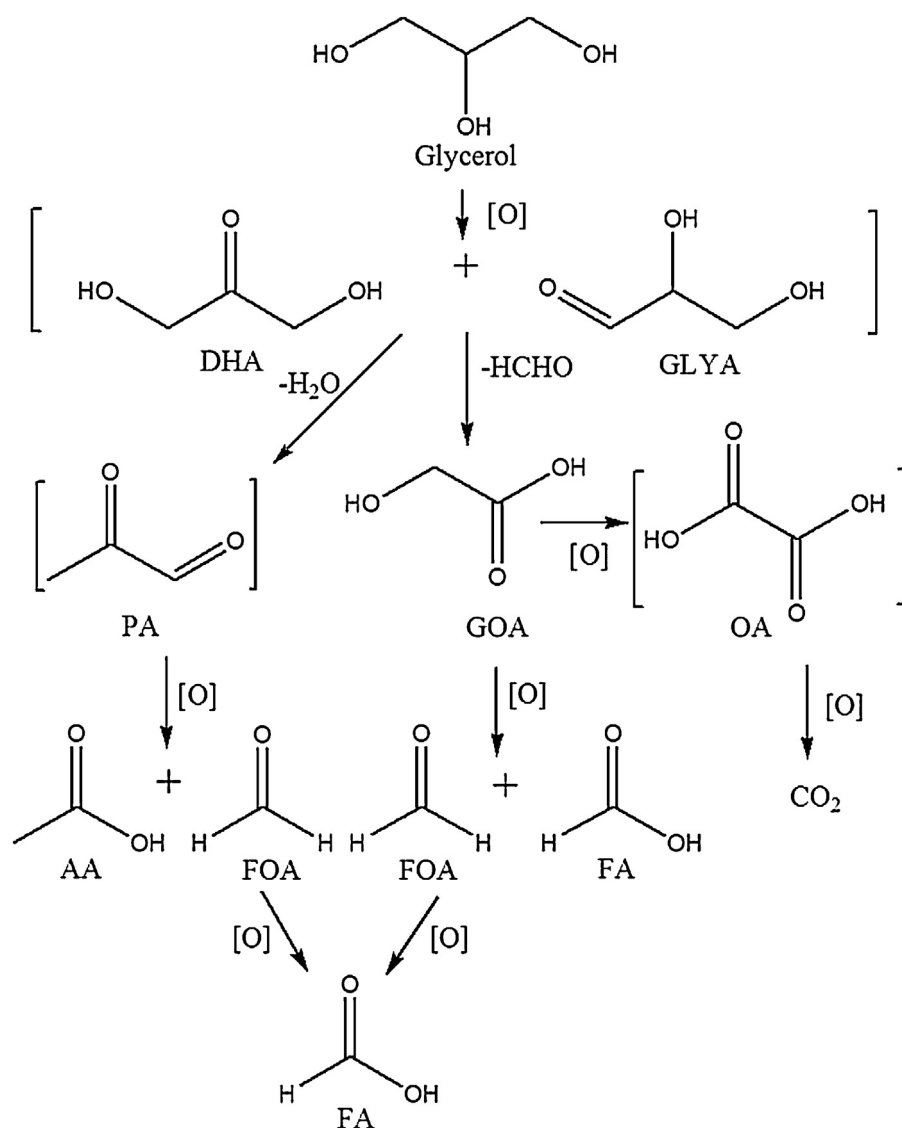
**Table 2**  
Oxidations catalysed by Ru(OH)<sub>4</sub>/r-GO and FeCl<sub>3</sub><sup>a</sup>.

Entry	Substrate	Conv. (%)	Yield (%)					TOC (ppm)
			FA	GOA	CO <sub>2</sub>	AA	FOA	
1	DHA	100.0	45.7	5.6	0.9	8.5	20.1	225.0
2	GLYA	100.0	42.0	2.6	0.9	1.8	46.7	147.0
3	GOA	74.3	31.1	7.4	ND	–	35.6	123.4
4	FOA	45.5	40.0	–	ND	ND	5.5	90.0
5	AA	0.0	ND	ND	ND	ND	0.0	191.9
6	FA	7.7	–	ND	ND	ND	7.7	88.4
7	OA	100.0	ND	ND	ND	ND	100	0.0
8	1,2-PO	57.9	7.7	19.1	8.7	ND	18.3	234.9
9	1,3-PO	89.3	50.0	3.8	2.9	2.4	28.2	206.2
10	EG	29.6	13.6	9.7	ND	0.3	5.1	181.8
11	Glyoxal	100.0	47.2	2.9	ND	11.0	38.1	118.3
12 <sup>b</sup>	DHA	100.0	27.6	4.2	19.0	7.3	31.4	197.0
13 <sup>c</sup>	DHA	100.0	41.1	6.4	1.1	14.4	33.5	191.1
14 <sup>b</sup>	GOA	49.6	13.4	4.4	ND	–	31.7	130.7
15 <sup>c</sup>	GOA	14.2	4.9	1.1	ND	–	7.1	177.8

<sup>a</sup> Reaction condition: substrate, 2 mmol; *T* = 160 °C; reaction time, 1 h; O<sub>2</sub> pressure, 0.5 MPa; substrate: Ru = 1000; FeCl<sub>3</sub> concentration, 40 mM.

<sup>b</sup> Without FeCl<sub>3</sub>.

<sup>c</sup> Without Ru(OH)<sub>4</sub>/r-GO.



**Scheme 1.** Possible pathway of glycerol oxidation to formic acid.

**Table 3**Oxidations of carbonates catalysed by Ru(OH)<sub>4</sub>/r-GO and FeCl<sub>3</sub><sup>a</sup>.

Entry	Substrate	Conv. (%)	Yield (%)				TOC (ppm)	
			FA	GOA	CO <sub>2</sub>			
1	Glucose	100.0	50.0	2.4	0.7	2.5	44.0	322.1
2	Fructose	100.0	45.7	3.6	1.0	3.2	45.8	311.8
3 <sup>b</sup>	Cellulose	–	20.3	1.2	1.7	0.5	12.2	226.9

<sup>a</sup> Reaction condition: substrate, 2 mmol; T = 160 °C; reaction time, 1 h; O<sub>2</sub> pressure, 0.5 MPa; substrate: Ru = 1000; FeCl<sub>3</sub> concentration, 40 mM.<sup>b</sup> Cellulose, 0.18 g; reaction time 5 h.

dehydrogenation, most of which are rapidly converted to GOA through eliminating FOA, and the other may be converted to PA via dehydration and rearrangement and further to AA and FOA via oxidation. Most of GOA is oxidized to FOA and FA, and the other is oxidized to OA and subsequently to CO<sub>2</sub> via further oxidation.

### 3.5. Oxidation of other carbonates

Inspired by the above results, we applied Ru(OH)<sub>4</sub>/r-GO and FeCl<sub>3</sub> in the oxidations of carbohydrates including glucose, fructose and cellulose, and the results are listed in Table 3. To our delight, FA with high yields around 50% was obtained from the oxidation of glucose and fructose (Table 3, entries 1 and 2), respectively, and a FA yield of 20% was obtained via the cellulose oxidation (Table 3, entry 3). This indicates that the combination of Ru(OH)<sub>4</sub>/r-GO and FeCl<sub>3</sub> is a robust catalytic system for the production of FA from biomass oxidation, which may have promising applications. The study on the reaction mechanism of the FA production from carbohydrate oxidation is under way in our group.

## 4. Conclusions

The production of formic acid from glycerol oxidation was achieved using Ru(OH)<sub>4</sub>/r-GO and FeCl<sub>3</sub> as the catalyst in aqueous solution, and high yields of formic acid around 60% was obtained. Ru(OH)<sub>4</sub>/r-GO and FeCl<sub>3</sub> displayed synergistic effects on the FA production from catalytic oxidation of glycerol though the reaction mechanism is not clear temporarily. The combination of Ru(OH)<sub>4</sub>/r-GO with FeCl<sub>3</sub> was also effective to selectively catalyse the oxidations of carbohydrates including glucose, fructose, cellulose directly to FA. The catalytic system represented here may find promising applications in the production of FA from the biomass oxidation, and further work is under way in our group.

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